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Radiative lifetimes and coherence lengths of one-dimensional excitons in single-walled carbon nanotubes

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We evaluated the radiative lifetimes and the one-dimensional exciton coherence lengths in single-walled carbon nanotubes (SWNTs). The radiative lifetimes determined from simultaneous measurements of photoluminescence (PL) lifetimes and PL quantum yields range from ~3 to 10 ns, and slightly increase with the tube diameter. The exciton coherence lengths in SWNTs are of the order of 10 nm, as deduced from the experimentally obtained radiative lifetimes, and they are about ten times larger than the exciton Bohr radius along the tube axis.

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The optical properties of single-walled carbon nanotubes (SWNTs) are of great interest from a fundamental physics perspective, but also because of their potential applications as novel light-emitting materials for future optoelectronic devices. Because the excited electrons and holes are strongly confined in one-dimensional (1D) systems, the dynamics of the correlated electron-hole pairs (excitons) dominates the optical properties in semiconducting SWNTs.[1,2] The exciton spatial coherence volume (length) is defined as the volume from which the exciton can coherently capture the oscillator strength.[3] The exciton radiative lifetimes and the photoluminescence (PL) quantum yields are therefore dominated by the coherence volumes (lengths).[3,4] Moreover, the coherence lengths in SWNTs also determine whether the exciton motion can be treated as diffusive or not, which is the issue under intense debate.[5–7] This is directly related to the exciton relaxation mechanism and nonlinear optical properties[8] and therefore crucial for the future application of SWNTs as photonics devices such as light-emitting transistors and quantum light sources.[9]

The coherence length L_c is closely related to the radiative lifetime τ_R and the homogeneous linewidth Δ.[3] τ_R can be estimated from the PL quantum yield η_{PL} and the PL decay time τ_{PL}. For SWNTs, several experimental[10–12] and theoretical[13,14] studies of τ_R have been reported. However, the measured values of τ_R in each study show large scatter from ~10 to 100 ns.[10–12] The sample-dependent large scatter in η_{PL} (0.01%–1%) for surfactant suspended SWNTs[10–12,15] has prevented us from determining τ_R and L_c from the experimental results.

In this Rapid Communication we investigated the exciton radiative lifetimes of SWNTs using highly isolated SWNT ensembles with high PL quantum yields (η_{PL} ~ 1%), and determined the exciton coherence lengths from the radiative lifetimes. We measured the PL lifetimes and PL quantum yields of various (n,m) SWNTs simultaneously. The experimentally determined radiative lifetimes are typically 3–10 ns at room temperature. From the radiative lifetimes, we revealed that the exciton spatial coherence extends ~10 nm along the tube axis.

The SWNTs were synthesized by the alcohol catalytic chemical vapor deposition method at 850 °C.[16] These SWNTs were isolated by dispersion in a toluene solution with 0.07 wt% poly[9,9-dioctylfluorenyl-2,7-diyl] (PFO) (PFO-dispersed SWNTs), 60 min of moderate bath sonication, 15 min of vigorous sonication with a tip-type sonicator, and centrifugation at an acceleration of 13 000 g for 5 min, according to the procedure developed by Nish *et al.*[17] For comparison, we also prepared SWNTs by dispersion in D_2O using 0.5 wt% sodium dodecyl benzene sulfonate (SDBS) (SDBS-dispersed SWNTs) with 30 min of vigorous sonication and ultracentrifugation at an acceleration of 150 000 g for 2 h, according to the procedure in Ref. 18.

We measured the PL lifetimes using the femtosecond excitation correlation (FEC) method. The FEC method has been successfully applied to a variety of materials, including SWNTs, to measure the recombination lifetimes of excitons.[19–21] In the FEC experiments, the SWNTs were excited with optical pulses from a Ti:sapphire laser of central wavelength 745 nm, repetition rate 80 MHz, pulse duration ~150 fs, and spectral width 8 nm. The two beams separated by the delay time τ were chopped at 800 and 670 Hz, respectively, and collinearly focused onto the same spot (~10 μm). Only the PL signal components modulated at the sum frequency (1470 Hz) were detected as FEC signals with a photomultiplier and a lock-in amplifier after dispersion of PL by a monochromator. The measurements were carried out under the excitation condition ~100 $\mu J/cm^2$. Detailed discussions on the PL lifetime measurement of SWNTs using FEC technique are presented in Ref. 20. The η_{PL} values of SWNTs were determined by comparison with those of the reference dyes (Styryl-13 and Rhodamine-6G).[15] The η_{PL} of Styryl-13 was calibrated against that of Rhodamine-6G in methanol (η_{PL}=95%).

Figure 1(a) shows the absorption spectra of PFO-dispersed SWNTs and SDBS-dispersed SWNTs. The underlying background in the absorption spectrum of PFO-dispersed SWNTs is remarkably suppressed compared to that of the SDBS-dispersed SWNTs, and the absorption peaks are much more pronounced. This indicates that bundled SWNTs, residual impurities, or other amorphous and graphitic carbons were not included in the PFO-dispersed sample. Figure 1(b) shows the PL excitation (PLE) map of PFO-dispersed SWNTs. The absorption spectra and PLE spectra show that

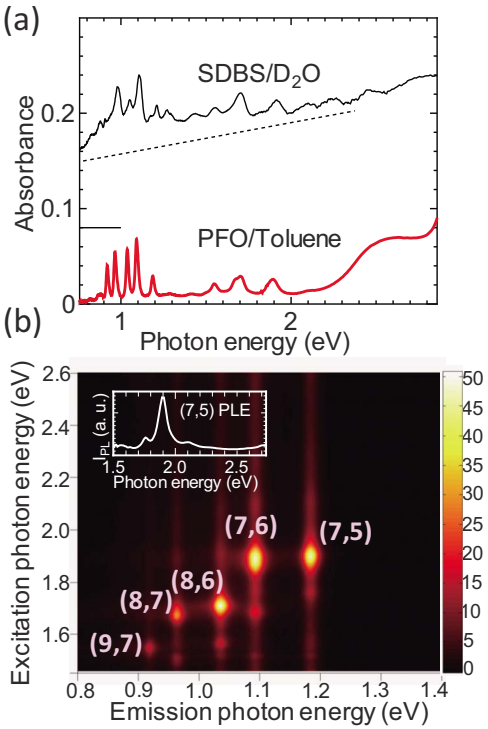

FIG. 1. (Color online) (a) Comparison of optical absorption spectra of SWNTs dispersed with SDBS in D_2O and PFO in toluene. (b) PL excitation map of PFO-dispersed SWNTs. Inset shows the PLE spectrum of (7, 5) SWNTs.

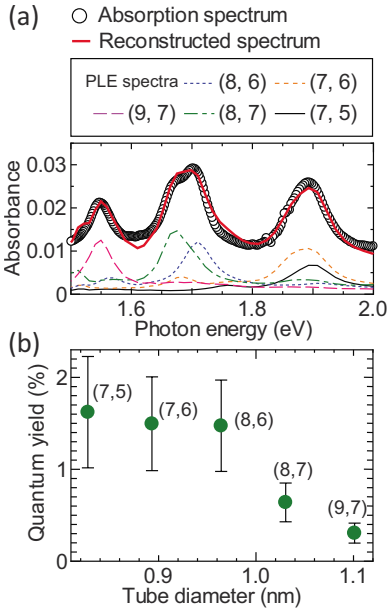

FIG. 2. (Color online) (a) Optical (circles) and decomposed (curves) absorption spectra of SWNTs with PFO in toluene using the PLE spectra of each (n,m) SWNT around the E_{22} transition. The red solid curve is the reconstructed absorption spectrum using PLE spectra of each (n,m). (b) Measured PL quantum yields of PFO-dispersed SWNTs as a function of tube diameter.

only several types of chiral indices were included in the PFO-dispersed SWNTs samples. The diameters of SWNTs in the sample estimated from the absorption and PLE spectra range from ~0.8 to 1.2 nm. The chiral indices of those peaks in the map are determined according to the assignment scheme described in Ref. 22.

In addition to the absorption spectrum with very low backgrounds, the small number of peaks enabled us to extract the η_{PL} of each (n,m) nanotube type in the PFO-dispersed sample. Figure 2(a) shows the absorption spectrum and the reconstructed spectrum based on the observed PLE spectrum. The reconstructed spectrum is the total of each (n,m) PLE spectrum, with only the amplitude of the peak varied as a fitting parameter. From the peak heights obtained in the fitting procedure, we determined the absorbance of each (n,m) peak at E_{22}. Figure 2(b) shows the evaluated η_{PL} of PFO-dispersed SWNTs as a function of tube diameter under the E_{22} resonance excitation conditions in each chiral index, where the relaxation rates from E_{22} to E_{11} were assumed to be independent of the chirality.[23] We estimated the η_{PL} to be from ~0.3% to ~1.6%, depending on the tube diameter. The relatively smaller diameter nanotubes have larger η_{PL} values, reaching ~1.6% for (7, 5) SWNTs. This is consistent with a previous report on PFO-dispersed CoMoCAT SWNTs.[17]

Figure 3(a) shows the FEC signals as a function of delay time for (7, 5) SWNTs. The upward direction on the vertical axis indicates that the FEC signals have a negative sign. We checked that the FEC decay curves did not change by the excitation power density in the range from ~20 to 300 $\mu J/cm^2$ [see inset of Fig. 3(a)]. The decay curve is closely described by a double exponential function (solid line) after subtracting the background signals. The exciton population showing double exponential decay as $N_1(t) = C\exp(-t/\tau_A) + (1-C)\exp(-t/\tau_B)$ $(0 \le C \le 1$ and $\tau_A < \tau_B)$ gives the FEC signal $I_C(\tau)$ as

$$I_C(\tau) \propto -[C\tau_A \exp(-\tau/\tau_A) + (1-C)\tau_B \exp(-\tau/\tau_B)], \quad (1)$$

where C is the fractional amplitude of the fast decay component.[20] Here, we define the effective PL lifetime as $\tau_{PL} = C\tau_A + (1-C)\tau_B$, and the ratio of the fast component Y_A as $Y_A = C\tau_A/[C\tau_A + (1-C)\tau_B]$. For (7, 5) SWNTs in Fig. 3(a), we obtained $Y_A \cong 0.7$, $\tau_A \cong 45$ ps, and $\tau_B \cong 200$ ps by the fitting procedure. These are similar to the recently reported values for single (6, 5) SWNTs in surfactant suspension.[24] The effective PL lifetime τ_{PL} is calculated as ~60 ps for (7, 5) SWNTs.[21] Figure 3(b) shows the effective PL lifetimes of PFO-dispersed SWNTs as a function of tube diameter. SWNTs with small diameters tended to have larger τ_{PL}.

Figure 4 shows the experimentally derived radiative lifetimes τ_R of SWNTs at room temperature as a function of tube diameter. The τ_R are calculated from η_{PL} in Fig. 2(b) and τ_{PL} in Fig. 3(b) as $\tau_R = \tau_{PL}/\eta_{PL}$. We found that the evaluated τ_R are typically ~3–10 ns, and slightly increase with the tube diameter. From the obtained radiative lifetime at room temperature, the oscillator strength and the coherence length L_c of the 1D exciton states in SWNTs can be deduced. Note that the experimentally observed radiative decay rate τ_R^{-1} does not simply correspond to that of the bright $K_{ex}=0$ exciton τ_0^{-1}, where K_{ex} is the exciton momentum. The oscillator strength of $K_{ex}=0$ exciton is shared by all states within

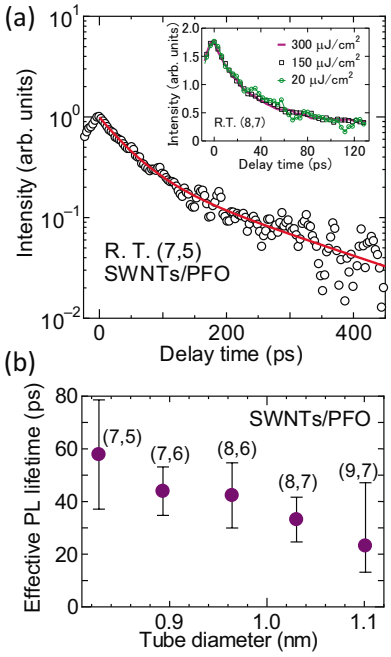

FIG. 3. (Color online) (a) The FEC signals for the (7, 5) SWNTs of the PFO-dispersed sample measured under 1.66 eV excitation at ~100 $\mu J/cm^2$. The red solid curve is given by a double exponential function. Inset shows the excitation power dependence of FEC curves for (8, 7) SWNTs from ~20 to 300 $\mu J/cm^2$. (b) The effective PL lifetimes τ_{PL} as a function of tube diameter in the PFO-dispersed samples. Only the τ_{PL} for the (9, 7) SWNTs was measured under 1.55 eV excitation to distinguish the PL signal of the (9, 7) SWNTs from that of the (8, 7) SWNTs.

the finite homogeneous linewidth $\Delta(T)$ due to the uncertainty of K_{ex} induced by dephasing process,[3] and here we define the oscillator strength reduced by dephasing process as F_x. In addition, both the thermalization within each single exciton band, and the exciton distribution among bright and dark exciton states further reduce the F_x to the effective oscillator strength $F_{x,eff}$. We can obtain $F_{x,eff}$ from the measured τ_R as

$$F_{x,eff} = \frac{1}{\tau_R}\frac{2\pi\varepsilon_0 m_0 \hbar^2 c^3}{n e^2 E_x^2}, \tag{2}$$

where n is the refractive index (~1.5 for toluene), m_0 is the electron mass, and E_x is the exciton energy.

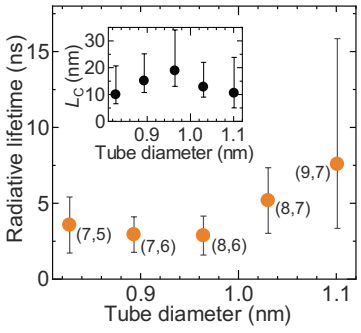

FIG. 4. (Color online) Determined radiative lifetimes τ_R of SWNTs as a function of tube diameter. Inset shows deduced coherence lengths L_c as a function of tube diameter.

The fraction of excitons $r_S(T)$ within $\Delta(T)$ among the thermalized excitons in the bright exciton band can contribute to radiative recombination. $r_S(T)$ is given by[3]

$$r_S(T) = \int_0^{\Delta(T)} D(E)e^{-E/k_BT}dE \Big/ \int_0^{\infty} D(E)e^{-E/k_BT}dE, \tag{3}$$

where $D(E)$ is the exciton density of states. For the 1D case, assuming $D(E) \propto 1/\sqrt{E}$, we obtain $r_S(T) = \mathrm{erf}(\sqrt{\Delta/k_BT}) \sim \sqrt{\Delta/k_BT}$. The $T^{-1/2}$ dependence of the radiative decay rate has been observed in the temperature dependence in the PL measurements.[25] As mentioned above, the exciton distribution between singlet bright and dark states decreases F_x again by a factor of[13,26]

$$r_M(T) = e^{-\delta_1/k_BT}/(1 + e^{-\delta_1/k_BT} + 2e^{-\delta_2/k_BT}), \tag{4}$$

where δ_1 and δ_2 are the energy differences of the bright exciton and higher dark excitons measured from the bottom of the lowest singlet dark exciton band, respectively. Since the relationship between $F_{x,eff}$ and F_x is expressed as $F_x = r_S^{-1} r_M^{-1} F_{x,eff}$ using $r_S(T)$ and $r_M(T)$, we thus determine the oscillator strength F_x from $F_{x,eff}$. Using experimentally obtained values of $\Delta(T) \approx 13$ meV for a single nanotube at room temperature,[27] $\delta_1 \approx 4$ meV,[28] and $\delta_2 - \delta_1 \approx 30$ meV,[29] we obtain the factor $r_S^{-1} r_M^{-1} \sim 6$ for (7, 5) SWNTs.

The F_x contains information on the exciton coherence length. The exciton coherence length L_c and the exciton oscillator strength F_x are related as $L_c = F_x/f_0|\phi(0)|^2$, where f_0 is the oscillator strength of a single k-state in the 1D momentum space, and $\phi(z_e - z_h)$ denotes the envelope function of the electron-hole relative motion. In the 1D case, $|\phi(0)|^2 \sim 1/a_x\sqrt{\pi}$, where a_x is the exciton Bohr radius (exciton size). Using the theoretical derived value of $a_x \approx 1.5$ nm (Ref. 30) and evaluating $f_0 \approx 5$ according to Ref. 31, we evaluate the coherence length of excitons as $L_c \sim 10$ nm in (7, 5) SWNTs.

Inset in Fig. 4 shows the evaluated coherence lengths for various (n,m) SWNTs. Here, we neglected the diameter dependence of $\delta_2 - \delta_1$ because of their small contribution. We found that each (n,m) type has similar values of $L_c \sim 10$ nm. These are in good agreement with the calculated values of L_c from the different formula using Δ and the exciton effective mass.[32]

From our results, we can comment on the motion of excitons in SWNTs: The previously observed exciton excursion range of ~100 nm (Ref. 7) is determined by the diffusive motion of the excitons because the $L_c \sim 10$ nm is much smaller than the excursion range. The L_c also gives the saturation density N_S of excitons in SWNTs as $1/N_S \sim L_c$.[32] From $L_c \sim 10$ nm, we get $N_S \sim 10^2$ excitons/μm and this value is the upper limit of the exciton density in SWNTs at room temperature, which leads to the strong optical nonlinearity of SWNTs. Our experimental determination of L_c thus provides the further insight of the exciton transport and optical properties in SWNTs.

In conclusion, we have studied the exciton radiative lifetimes and coherence lengths in SWNTs. The radiative lifetimes of excitons at room temperature were experimentally

determined as 3 ~ 10 ns depending on the tube diameter. We found that the exciton coherence lengths were ~10 nm along the tube axis.

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